

## ULTRAVIOLET EFFECTS ON HIGH POLYMERS AND THEIR RELATION TO RADIATION CHEMISTRY \*

by Gerald Oster

Polytechnic Institute of Brooklyn  
Brooklyn, New York.

Although ionizing radiation sources produce energies in the range  $10^3$ - $10^6$  ev the ultimate chemical effects of such radiation only involve cleavages of chemical bonds, i.e., energies of about 5 ev (equivalent to about 100 kilocal/mole). The high energy photoelectrons which are produced in the initial act quickly lose most of their energy to the medium. The energy has been ultimately utilized to heat the medium and to chemically convert some of the irradiated material.

The chemical reaction could be the immediate result of some ionization process or of an electronic excitation. Direct evidence of the chemical manifestation of ionization processes have not been forthcoming. The ionization process of concern here is not that encountered in ionic polymerization, the latter being really a radical ion. The evidence for electronic excitation is, however, quite clear. The manner of electronic excitation need not be direct. In the liquid scintillation counter the ionizing radiation is absorbed mainly by the solvent which is usually in considerable excess. Energy is transferred through the medium to the solute which fluoresces when excited. The solvent must be of an aromatic nature if it is to serve as a good energy transfer medium. Certain substances, which of themselves are not fluorescence quenchers, can suppress the scintillating properties of the solution by interrupting the energy transfer process.<sup>1</sup>

Excitation to higher states may not be of great importance in radiation chemistry since extremely rapid internal conversions during about  $10^{-12}$  sec. allow the levels to cascade to the first electronically excited state. This latter state may have a lifetime of the order of  $10^{-9}$  sec. and is most closely connected with chemical transformations. A fundamental question in radiation chemistry is to establish what portion of the absorbed energy appears as electronic excitation.

Ultraviolet light in the 5 ev range (250m $\mu$ ) can electronically excite many organic compounds. Hence if photochemical studies using ultraviolet light were carried out in parallel with ionizing radiation studies one should be able to ascertain the role of electronic excitation in radiation chemistry.

Precisely parallel experiments cannot be carried out because the ultraviolet absorbing system must contain some sensitizing constituent. The chemical reaction is one between excited sensitizer and the medium. With ionizing radiation, however, any molecules in the system absorb the

\* Presented at the National Meeting of the Japan Chemical Society, April 4, 1960 at Waseda University.

# Contrails

energy and the chemical reaction may differ from that with ultraviolet light.

Polyethylene can be crosslinked with ionizing radiation.<sup>2</sup> The reaction is accompanied by the evolution of hydrogen gas. The crosslink is apparently formed when hydrogen atoms are abstracted from adjacent chains. The double bonds which occur in about equal number<sup>3</sup> probably arise from hydrogen abstraction on adjacent positions on the same chain. Some degradation of the polymer on scission of the main chain backbone can also occur.<sup>4</sup>

Polyethylene can also be crosslinked by ultraviolet light of wavelength 200-300 $\mu$ .<sup>5</sup> In practice it is simplest to employ as a light source the commercially available mercury resonance lamp which produces mainly 254 $\mu$ . The crosslinking may be carried out with irradiation of short duration if benzophenone is used as the sensitizer. The crosslinked polymer thus produced possesses less double bonds than has the polymer which had been crosslinked by ionizing radiation.<sup>6</sup>

With ionizing radiation crosslinking should be fairly uniform throughout the polymeric material. With ultraviolet light, on the other hand, crosslinking should be confined to the regions where the sensitizer is located, *i.e.*, to the amorphous regions of the material. This has a number of interesting consequences. Thus we find<sup>7</sup> that very small amounts of crosslinking will inhibit the crystal growth which occurs when high density polyethylene is kept at 80°C. Similarly for low density polyethylene the rate of crystallization at room temperature is likewise inhibited when the material is crosslinked by ultraviolet light.<sup>7</sup> Subtle differences in ultrastructure in polyethylenes are exaggerated when mechanical tests are made on the materials at elevated temperatures (Fig. 1). In this case for the lower extents of crosslinking there are great differences in zero strength time (the time for the material to support a given load before breaking) between the low density material (DYNH) and the high density material (Marlex). Studies of these kinds combined with careful electron micrograph studies to determine ultrastructure should be extremely interesting.

The mechanism of the ultraviolet crosslinking phenomenon is not well understood at the present time. Recent studies in this laboratory show that at temperatures below about -25°C although the sensitizer, benzophenone, is photolyzed no crosslinking occurs. Apparently, a heat of activation is involved in the hydrogen abstraction. Furthermore, the product produced at low temperatures has an ultraviolet spectrum which differs from that produced at room temperature. Our studies indicate that the production of the low temperature material is in competition with the crosslinking reaction. In this connection we might remark that crosslinking occurs best when oxygen is present.<sup>8</sup> The only extractable material we have been able to identify is benzoic acid which is obviously a photooxidation product of benzophenone.

Another striking difference between ionizing radiation and ultraviolet light is that chain scission is considerably less or even nonexistent in the latter method. For example, polymethyl methacrylate is severely degraded by ionizing radiation, as are all polymers with two substituents on the same carbon atom. With ultraviolet light using

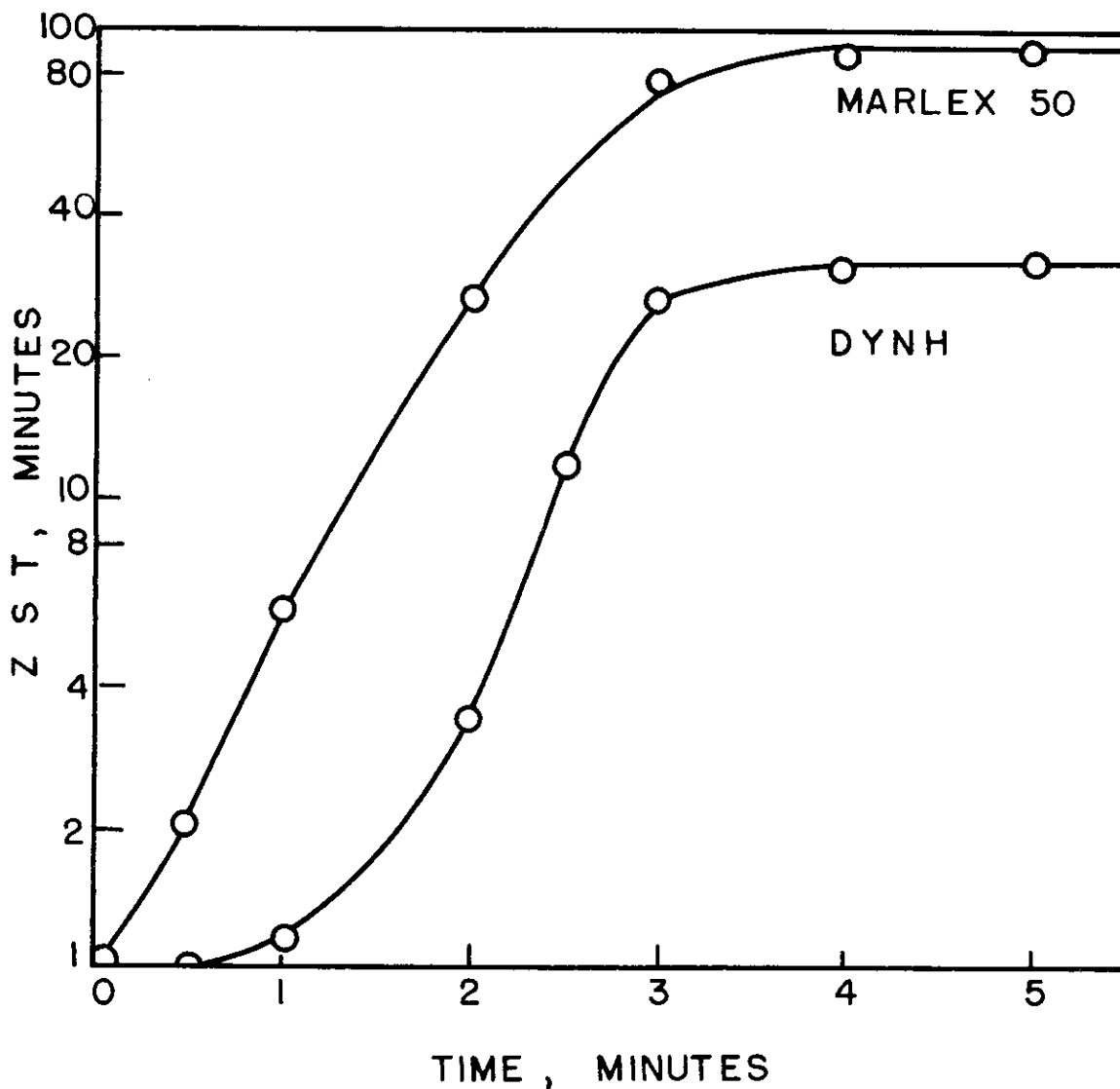
# Contrails

benzophenone, on the other hand, the polymer is crosslinked.<sup>5</sup> This distinction is brought out dramatically by means of electron spin resonance where the spectra for the products produced by the two different types of radiation differ enormously.<sup>9</sup> It may be that ionization of the doubly substituted carbon atom leads to instability of the carbon-carbon bond whereas such a reaction cannot occur with ultraviolet light because it is energetically too weak.

The ultraviolet light crosslinking reactions described above are superficially related to the effects of ionizing radiation. What I have tried to show, however, is that the differences are more interesting and their study may lead to a better understanding of the chemical reactivity and structure of high polymers as well as providing a better understanding of radiation chemistry itself.

## REFERENCES

1. H. Kallmann and M. Furst, Phys. Rev., 72, 857 (1950).
2. A. Charlesby, Proc. Roy. Soc. (London) A215, 187 (1952).
3. M. Dole, C. D. Keeling, and D. G. Rose, J. Amer. Chem. Soc., 76, 4304 (1954); Compare with A.A. Miller, E.J. Lawton and J.S. Balwit, J. Phys. Chem., 60, 599 (1956).
4. R. M. Black and B.J. Lyons, Nature, 180, 1346 (1957).
5. G. Oster, G.K. Oster, and H. Moroson, J. Polymer Sci., 34, 671 (1959).
6. C.A. Grace and A. Charlesby, Paper IC 7, Symp. Makromol., Wiesbaden, October 1959.
7. I. Uematsu, Rep. Prog. Polymer Phys. Japan, (Tokyo Metropolitan Univ.), 2, 114 (1959).
8. Private Communication from Prof. S. Shida (Tokyo Inst. Technol.).
9. Private Communication from Prof. S. Okamura and Mr. Nishida (Kyoto Univ.).



**FIG.1 - ZERO STRENGTH TIME VS. IRRADIATION TIME - SENSITIZED WITH BENZOPHENONE**

# *Contrails*